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## Description

The present invention relates to an improved process for producing antimonate-based catalysts and the improved catalysts so made.

Antimonate redox catalysts, that is redox catalysts in which the antimonate moiety forms the basic anionic structure of the system, are well known. They are exemplified, for example, in US—A—3,341,292 and US—A—3,338,952.

Usually, such catalysts are made by slurry techniques wherein source compounds containing the elements to be incorporated into the catalysts such as nitrates, oxides, acids and the like are combined in the form of a slurry, the liquid removed from the slurry to form a pre-catalyst and the pre-catalyst heated at elevated temperature to form the desired catalyst.

In order to impart strength (attrition resistance), it is customary to include in the catalyst a suitable support material. Silica, alumina, titania, zirconia and so forth are customarily used for this purpose. During catalyst preparation, these support materials are simply combined with the other source compounds in forming the pre-catalyst slurry.

In accordance with the invention, it has now been discovered that antimonate catalysts, exhibiting superior catalytic properties and superior attrition resistance can be produced if the support material is composed of the combination of a catalyst support material derived from a sol and a fumed catalyst support material.

Thus, the present invention provides an improvement in the known single slurry process for producing a fluid bed catalyst comprising an antimonate-based oxide complex supported on a catalyst support in which (1) source compounds containing all of the elements of the oxide complex and the support material are combined to form a pre-catalyst slurry, (2) the liquid of the slurry is removed therefrom to form a pre-catalyst and (3) the pre-catalyst is heated at elevated temperature to form the catalyst, which improvement consists in that the support material combined with the source compounds in step (1) is composed of a fumed catalyst support material and a catalyst support material sol.

### Detailed description

#### Antimonate-based oxide complex catalyst

The present invention is applicable to the production of various antimonate-based redox catalysts. By "antimonate-based redox catalyst" is meant a catalyst which itself continuously gains and loses oxygen during the reaction and further in which the antimonate moiety forms the basic anionic structure of the material. Basically, such materials are metal antimonates wherein the metal is Fe, Sn, U, Th, Cr, Ti, Ce and/or Mn. Various additional promoters may be included in these systems, but usually the amount of promoter, if present, is less than twenty-five atom

percent based on the amount of metal antimonate in the system.

These catalysts are well known in the art and described, for example, in US—A—3,431,292 US—A—3,338,952 US—A—3,773,692, US—A—4,083,804 and GB—A—2,009,613.

Normally, the antimonate redox catalyst to which the invention relates will correspond to the following empirical formula:



wherein

A is Fe, U, Sn, Th, Cr, Ti, Ce, Mg and/or Mn; and B is Zr, V, W, Mo, As, B, Cu, Pr, Al, Te, rare earth metals, alkali metals, alkaline earth metals other than Mg and/or Bi, and further; wherein

a is greater than 0 to 10, preferably 0.1 to 10;

b is 0 to 10, preferably 0.01 to 10;

c is 0.1 to 40, preferably 0.1 to 20; and

when A is other than Sn and/or Ti  $a+b < c$

x is a number determined by the valence requirements of the other elements present.

In such catalysts the ratio b:a is usually 1:10 to 2:1, preferably 3:10 to 8:10 and  $4b = a + c$ . Also Fe and Sn are the preferred A components. Preferably  $a + b < c$  in those catalysts in which A is other than Sn and/or Ti.

Preferably the ratio b/c is 5/10 to 1/10 and more preferably 2/10 to 4/10.

As is well known, antimonate-based catalysts can contain various other anionic-acting elements such as molybdenum and tungsten. However, in such instances the molybdenum and/or tungsten is present only as a promoter. To this end, the amount of molybdenum and/or tungsten present in an antimonate-based catalyst is normally less than 50 atom %, more typically less than 15% and even more typically less than 10% of the antimony content. This is merely a reflection of the fact that the catalyst are antimonate catalyst and not molybdates or tungstates.

#### Support materials

In accordance with the present invention, both the catalytic properties and the attrition resistance of fluid bed antimonate redox catalysts are improved by employing as the catalyst support the combination of a sol-derived catalytic support material and a fumed catalytic support material.

Both of these catalytic support materials are well known in the art and commercially available. A "sol-derived" catalytic support material is a catalytic support material which is available in the form of a colloidal slurry in a suitable liquid such as water. Silica sols are good examples of such materials. In addition to silica, other conventional support materials such as alumina, titania, zirconia and so forth are also available in sol form. Any such colloidal support material sol can be employed in accordance with the invention, although silica is preferred.

Fumed catalytic support materials are also well known. Basically, they are formed by an igneous process wherein a precursor compound is pyro-

lytically decomposed to form the support material.

A good example of such material is fumed silica, which is a very fine silica produced by reacting silicon tetrachloride with hydrogen and oxygen in a flame. This material is more fully described in *Encyclopedia of Chemical Technology*, 2nd. ed., Kurt Othmer, vol. 18, page 63. Fumed silica may be purchased under the trade name Aerosil or Carbosil. In addition to silica, other conventional support materials such as titania, zirconia, alumina and the like are also available in fumed form.

In carrying out the present invention, the sol derived catalytic support material and the fumed catalytic support material may have the same or different compositions. Preferably, their compositions are the same. In a particularly preferred embodiment, silica sol and fumed silica are employed to form the support.

The relative amounts of the two different support materials can vary widely and essentially any amounts can be used. Normally, the amount of each component will be at least 5% based on the total weight of the support. More typically, each type of support material will be present in an amount of at least 10%, more preferably at least about 25% by weight, based on the combined weight of the support material. In a particularly preferred embodiment of the invention, the support system of the catalyst is composed of about 10 to 40% fumed silica the balance being silica sol, measured on a silica weight basis.

#### Catalyst preparation technique

The catalysts of the invention are preferably formed in accordance with the conventional single slurry catalyst preparation technique. In this technique, source compounds such as nitrates, oxides, acids, anhydrides and the like containing all of the elements in the active catalytic material of the ultimate catalyst plus the support material are combined together in the form of a pre-catalyst slurry, the liquid phase of which is usually water. Next, the liquid is removed from the slurry to form a solid or gel pre-catalyst containing all of the components of the objective catalyst. The pre-catalyst is then heated at elevated temperature usually in the presence of air to decompose the source compounds and form the ultimate catalyst.

In this process, only a single aqueous slurry, the pre-catalyst slurry, need be formed. It is thus much simpler than other catalyst preparation processes such as two slurry step processes in which prior to making the pre-catalyst slurry a first slurry containing some but not all of the components of the catalyst is produced, the solids recovered therefrom and the solids mixed with other source compounds to form the pre-catalyst slurry.

The catalysts of the invention may also be made by a multi-slurry technique wherein more than one slurry is formed during catalyst preparation, although this is not preferred. See, for

example, US—A—4,280,929, which shows a multi-slurry technique for making a molybdate-based catalyst in which both fumed silica and a silica sol are used as a catalyst support. However in that patent it is essential that a first sol containing fumed silica and at least some of the components of the active catalytic material be dried to recover a solid and this solid then reslurried in a second slurry (pre-catalyst slurry) containing all of the catalyst ingredients. This technique is not used according to the present invention. Specifically, if a multi-slurry technique is used for catalyst preparation, then catalyst preparation is accomplished without adding to the pre-catalyst slurry a slurry-derived solid containing fumed silica and an active-component of the ultimate catalyst.

In a particularly preferred embodiment of the invention, the two different types of support material are premixed prior to combining with the other source compounds of the catalyst. This is particularly convenient on a commercial scale since a mixture of the two different support materials can be formulated in a separate location, for example, as by the support material manufacturer, and incorporated into the pre-catalyst slurry at the catalyst preparation plant.

Once the pre-catalyst slurry is formed in accordance with the present invention, it is processed in a conventional way to yield the catalysts of the invention. Specifically, the liquid is removed from the slurry as by filtration and/or evaporation to recover a pre-catalyst solid or gel, and the pre-catalyst is calcined at elevated temperature to form the objective catalyst.

#### Utility

The catalysts produced by the present invention are useful in various redox reactions. They find particular application in the ammoxidation of propylene or isobutylene to produce acrylonitrile and methacrylonitrile and the oxidation of olefins to produce unsaturated aldehydes and acids.

In order that the invention may be more fully understood the following examples are given by way of illustration only:

#### Comparative Example

A catalyst having a formula essentially the same as Catalyst 4 in GB—A—2009613 (40% by weight total silica) was prepared in the following manner. Ammonium tungstate, ammonium vanadate and ammonium molybdate were dissolved in water to form a first solution. A second solution comprising water acidified with  $\text{HNO}_3$  and containing  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3$  and tellurium oxide dissolved therein was also prepared. A 40% silica sol (Nalco) diluted with an equal amount of water was mixed with the nitrate solution followed by the addition of antimony oxide. To the resultant slurry was added the W/V/Mo solution and the composition so obtained was neutralized with ammonium hydroxide to a pH of about 2.3. The slurry was

digested and then dried and heated in air at 290°C for three hours, 425°C for three hours and 785°C for about two hours.

The catalyst was then charged into 1 1/2 inch (3.81 cm) inside diameter fluid bed reactor and contacted with a feed comprising 1 propylene/1.05 NH<sub>3</sub>/10 air at a WWH (weight propylene per unit weight catalyst per hour) of 0.10. The gross reaction product was recovered and analyzed. Acrylonitrile was produced with a yield (moles acrylonitrile produced per mole propylene fed×100) of 67.7% and the HCN yield was 4.1%.

#### Example 1

Comparative Example A was repeated except that 1/4 of the Nalco silica sol was replaced with fumed silica (on a silica weight basis). The catalyst obtained was tested in the same way as Comparative Example A and was found that acrylonitrile was produced with yields of 70.1% and HCN with yields of 4.9%.

The above examples show that the catalytic

properties of catalysts produced in accordance with the invention and particularly the ability of the catalyst to produce useful products based on the amount of propylene fed is enhanced when the catalyst is made in accordance with the inventive technique.

#### Comparative Example B and Examples 2 to 4

Comparative Example A and Example 1 were repeated in a series of experiments in which the relative amounts of the silica sol and the fumed silica in the catalyst were varied. The product catalysts were then subjected to a standard attrition resistance test wherein a suitably sized fraction of each catalyst was vigorously agitated in a tube equipped by an air jet. The amount of catalyst entrained in the air flow passing out of the tube indicates the percent attrition. Each catalyst was agitated for twenty hours with an attrition test being conducted after five hours and again after twenty hours. The results are set forth in the following table:

TABLE 1  
Support Material                      % Attrition

Example	% Silica sol	% Fumed silica	5 Hrs.	20 Hrs.
B	100	0	13.8	16.0
2	75	25	14.0	11.6
3	50	50	12.7	2.0
4	25	75	3.6	0.0

From the foregoing table, it can be seen that the attrition resistance of the catalysts significantly increases when two different types of silica are used to form the support.

#### Claims

1. A slurry process for producing a fluid-bed catalyst comprising an antimonate-based oxide complex supported on a catalyst support in which (1) source compounds containing all of the elements of said oxide complex and said support material are combined to form a pre-catalyst slurry, (2) liquid is removed from said pre-catalyst slurry to form a pre-catalyst, and (3) said pre-catalyst is heated at elevated temperature to form said catalyst, characterised in that the support material combined with said source compounds in step (1) is composed of (a) a fumed catalyst support material and (b) a catalyst support material sol said pre-catalyst slurry being formed without the addition of a slurry-derived solid containing fumed catalyst support material and one or more of said source compounds.

2. A process as claimed in Claim 1 characterised in that the process is a single-slurry process.

3. A process as claimed in Claim 1 or Claim 2 in which the fumed catalyst support material is

fumed silica and the catalyst support material sol is a silica sol.

4. A process as claimed in Claim 3 characterised in that the fumed silica and the silica sol are mixed together prior to being combined with the source compounds.

5. A process as claimed in any of Claims 1 to 4 characterised in that the antimonate-based oxide complex which is produced has the formula



wherein

A is Fe, U, Sn, Th, Cr, Ti, Ce, Mg and/or Mn; and B is Zr, V, W, Mo, As, Bi, Cu, Pr, Al, Te, rare earth metals, alkali metals, alkaline earth metals other than Mg and/or Bi, and further; wherein

a is greater than 0 to 10;

b is 0 to 10;

c is 0.1 to 40; and

when A is other than Sn and/or Ti,  $a+b < c$  x is a number determined by the valence requirements of the other elements present.

6. A process as claimed in Claim 5 characterised in that a is 0.1 to 10, b is 0.01 to 10 and c is 0.1 to 20.

7. A process as claimed in Claim 6 characterised in that  $4b = a + c$ .

8. A process as claimed in Claim 7 characterised in that A is Fe and/or Sn.

9. A process as claimed in Claim 8 characterised in that b/c is 1/10 to 5/10.

10. A process as claimed in Claim 9 characterised in that b/c is 2/10 to 4/10.

11. A multi-slurry process for producing a fluid-bed catalyst comprising an antimonate-based oxide and complex supported on a catalyst support in which (1) source compounds containing all of the elements of said oxide complex and said support material are combined to form a pre-catalyst slurry, (2) liquid is removed from said pre-catalyst slurry to form a pre-catalyst, and (3) said pre-catalyst is heated at elevated temperature to form said catalyst, characterised in that the support material combined with said source compounds in step (1) is composed of (a) a fumed catalyst support material and (b) a catalyst support material sol, said pre-catalyst slurry being formed without the addition of a slurry-derived solid containing said fumed catalyst support material and one or more of said source compounds.

12. A catalyst produced by a process as claimed in any of Claims 1 to 11.

#### Patentansprüche

1. Ein Aufschlammungsverfahren zur Herstellung eines Fließbettkatalysators, bestehend aus einem Oxidkomplex auf Antimonat-Basis auf einem Katalysatorträger in dem (1) eine alle die Elemente des Oxidkomplexes enthaltenden Grundsubstanzen und das Trägermaterial unter Bildung einer Katalysatorvorproduktaufschlammung zusammengegeben werden (2) Flüssigkeit aus dieser Katalysatorvorproduktaufschlammung unter Bildung eines Katalysatorvorproduktes entfernt wird und (3) dieses Katalysatorvorprodukt bei erhöhter Temperatur unter Bildung dieses Katalysators erhitzt wird, dadurch gekennzeichnet, daß das Trägermaterial, das mit den Grundsubstanzen in Stufe (1) zusammengegeben wird, aus (a) einem geschäumten Katalysatorträgermaterial und (b) einem Katalysatorträgermaterial-Sol besteht, wobei diese Katalysatorvorproduktaufschlammung ohne Zugabe eines Feststoffes aus der Aufschlammung gebildet wird, die das geschäumte Katalysatorträgermaterial und eine oder mehrere dieser Grundsubstanzen enthält.

2. Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß das Verfahren ein solches ist, bei dem eine einzelne Aufschlammung gebildet wird.

3. Verfahren gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß das geschäumte Katalysatorträgermaterial geschäumte Silika ist und das Katalysatorträgermaterial-Sol ein Silika-Sol ist.

4. Verfahren gemäß Anspruch 3, dadurch gekennzeichnet, daß das geschäumte Silika und das Silika-Sol zusammengegeben werden, bevor sie mit den Ausgangsmaterialien kombiniert werden.

5. Verfahren gemäß Anspruch 1 bis 4, dadurch gekennzeichnet, daß der hergestellte Oxidkomplex auf Antimonat-Basis der Formel



entspricht, worin

A Fe, U, Sn, Th, Cr, Ti, Ce, Mg und/oder Mn ist; und

B Zr, V, W, Mo, As, B, Cu, Pr, Al, Te, die seltenen Erdmetalle, Alkalimetalle, Erdalkalimetalle verschieden von Mg und/oder Bi und andere sind; worin

a größer als 0 bis 10;

b 0 bis 10;

c 0,1 bis 40; und,

sofern A von Sn und/oder Ti verschieden ist,  $a+b < c$  ist, und

x eine Zahl ist, die sich aus den Wertigkeitsanforderungen der anderen anwesenden Elemente ergibt.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß a 0,1 bis 10, b 0,01 bis 10 und c 0,1 bis 20 ist.

7. Verfahren gemäß Anspruch 6, dadurch gekennzeichnet, daß  $4b = a + c$  ist.

8. Verfahren gemäß Anspruch 7, dadurch gekennzeichnet, daß A Fe und/oder Sn ist.

9. Verfahren gemäß Anspruch 8, dadurch gekennzeichnet, daß b/c 1/10 bis 5/10 ist.

10. Verfahren gemäß Anspruch 9, dadurch gekennzeichnet, daß b/c 2/10 bis 4/10 ist.

11. Ein Verfahren mit vielen Aufschlämmungen zur Herstellung eines Fließbettkatalysators umfassend einen Oxidkomplex auf Antimonat-Basis, getragen auf einem Katalysatorträgerstoff, wobei (1) Grundsubstanzen, die alle der Elemente dieses Oxidkomplexes und dieses Trägermaterials enthalten, unter Bildung einer Katalysatorvorproduktaufschlammung zusammengegeben werden, (2) Flüssigkeit aus dieser Katalysatorvorproduktaufschlammung unter Bildung eines Katalysatorvorproduktes entfernt wird, und (3) dieses Katalysatorvorprodukt auf erhöhte Temperatur unter Bildung dieses Katalysatorvorproduktes auf erhöhte Temperatur unter Bildung dieses Katalysators erhitzt wird, dadurch gekennzeichnet, daß das Trägermaterial kombiniert mit diesen Grundsubstanzen in Stufe (1) zusammengesetzt ist aus (a) einem geschäumten Katalysatorträgermaterial und (b) einem Katalysatorträgermaterial-Sol, wobei diese Katalysatorvorproduktaufschlammung ohne Zugabe eines Feststoffes aus der Aufschlammung gebildet wird, welches dieses geschäumte Katalysatorträgermaterial und eine oder mehrere dieser Grundsubstanzen enthält.

12. Ein Katalysator hergestellt nach einem der Verfahren gemäß Ansprüchen 1 bis 11.

#### Revendications

1. Procédé en bouillie pour produire un catalyseur en lit fluidisé, comprenant un complexe d'oxyde à base d'antimoniate supporté sur un

support de catalyseur, dans lequel (1) des composés sources contenant tous les éléments dudit complexe d'oxyde et ladite matière de support sont combinés pour former une bouillie de pré-catalyseur, (2) du liquide est éliminé de ladite bouillie de pré-catalyseur pour former un pré-catalyseur, et (3) ledit pré-catalyseur est chauffé à température élevée pour former ledit catalyseur, caractérisé par le fait que la matière de support combinée avec lesdits composés sources à l'étape (1) est composée (1) d'une matière de support de catalyseur fumée et (b) d'un sol de matière de support de catalyseur, ladite bouillie de pré-catalyseur étant formée sans addition d'un solide dérivant d'une bouillie et contenant de la matière de support de catalyseur fumée et un ou plusieurs desdits composés sources.

2. Procédé selon la revendication 1, caractérisé par le fait que la procédé est un procédé à bouillie unique.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel la matière de support de catalyseur fumée est de la silice fumée et le sol de matière de support de catalyseur est un sol de silice.

4. Procédé selon la revendication 3, caractérisé par le fait que le silice fumée et le sol de silice sont mélangés avant d'être combinés avec les composés sources.

5. Procédé selon l'une des revendications 1 à 4, caractérisé par le fait que le complexe d'oxyde à base d'antimoniate qui est produit a la formule



dans laquelle

A est Fe, U, Sn, Th, Cr, Ti, Ce, Mg et/ou Mn; et

B est Zr, V, W, Mo, As, B, Cu, Pr, Al, Te, des métaux de terres rares, des métaux alcalins, des métaux alcalino-terreux autres que Mg et/ou Bi, et, en outre, dans laquelle

a est supérieur à 0 à 10;

b est compris entre 0 et 10;

c est compris entre 0,1 et 40; et

lorsque A est autre que Sn et/ou Ti,  $a+b < c$   
x est un nombre déterminé par les exigences de valence des autres éléments présents.

6. Procédé selon la revendication 5, caractérisé par le fait que a est 0,1 à 10, b est 0,01 à 10 et c est 0,1 à 20.

7. Procédé selon la revendication 6, caractérisé par le fait que  $4b = a + c$ .

8. Procédé selon la revendication 7, caractérisé par le fait que A est Fe et/ou Sn.

9. Procédé selon la revendication 8, caractérisé par le fait que b/c est 1/10 à 5/10.

10. Procédé selon la revendication 9, caractérisé par le fait que b/c est 2/10 à 4/10.

11. Procédé multi-bouillie pour produire un catalyseur en lit fluidisé comprenant un complexe d'oxyde à base d'antimoniate supporté sur un support de catalyseur dans lequel (1) des composés sources contenant tous les éléments dudit complexe d'oxyde et ladite matière de support sont combinés pour former une bouillie de pré-catalyseur, (2) du liquide est éliminé de ladite bouillie de pré-catalyseur pour former un pré-catalyseur, et (3) ledit pré-catalyseur est chauffé à température élevée pour former ledit catalyseur, caractérisé par le fait que la matière de support combinée auxdits composés sources à l'étape (1) est composée (a) d'une matière de support de catalyseur fumée et (b) d'un sol de matière de support de catalyseur, ladite bouillie de pré-catalyseur étant formée sans addition d'un solide dérivant d'une bouillie et contenant ladite matière de support de catalyseur fumée et un ou plusieurs desdits composés sources.

12. Catalyseur produit par un procédé suivant l'une des revendications 1 à 11.